

(12) LEVEL II

NSWC TR 80-111

AD A092796

**AN INVESTIGATION OF THE SHIPP
HEXANITROSTILBENE (HNS) PROCESS**

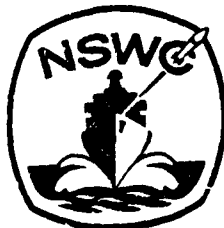
BY ELEONORE G. KAYSER

RESEARCH AND TECHNOLOGY DEPARTMENT

25 AUGUST 1980

Approved for public release, distribution unlimited.

DTIC
ELECTE
DEC 9 1980
S B D



NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910

FILE COPY

80 12 09 019

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
NSWC TR-80-111	AD-A192716	
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
An Investigation of the Shipp Hexanitrostilbene (HNS) Process		Final Report
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s)
Eleonore G. Kayser		
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Naval Surface Weapons Center White Oak, Silver Spring, Maryland 20910		NASA; R122B; SSPO; R12KU
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
		25 August 1980
		13. NUMBER OF PAGES
		30
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
HNS Hexanitrostilbene HPLC Analysis of Explosives Product Analysis of the HNS (Shipp) Process		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>→ This report describes the separation, characterization, and analysis of the products which the Shipp hexanitrostilbene (HNS) process yields. In this process, trinitrotoluene (TNT), dissolved in a mixture of tetrahydrofuran (THF) and methanol (MeOH), is reacted with commercial bleach (NaOCl) to form HNS. The isolated products include: hexanitrostilbene (HNS), and</p>		

DD FORM 1473

JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
11-0122-LE-014-6501

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

41143

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. (continued)

→ hexanitrobibenzyl (HNBiB), trinitrobenzene (TNB), trinitrobenzoic acid (PiCOOH), trinitrobenzaldehyde (PiCHO), trinitrobenzyl chloride (PiCH₂Cl), picryl chloride (PiCl), picric acid (PiOH), trinitrobenzyl alcohol (PiCH₂OH), 4,6-dinitro-2,1-benzisoxazole (Anil), and trichloronitromethane (chloropicrin) as well as some unreacted TNT. Approximately 5-10% of the red-tar fraction of the reaction mixture remains unidentified. Solvent effects on the yield of several of the above by-products are discussed; however, no other solvent examined displayed the pronounced specificity of tetrahydrofuran (THF) for this reaction.

↗

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

FOREWORD

This report describes the identification, characterization, and analysis of several of the by-products of the Shipp hexanitrostilbene (HNS) process. This work was sponsored by the Strategic Systems Project Office under Task B00035B001;R12 KU and the Lyndon B. Johnson Manned Spacecraft Center under Task NASA R12ZB. The identification of vendors or commercial products implies neither criticism nor endorsement by the Naval Surface Weapons Center.

Elihu Zimet

ELIHU ZIMET
By direction

Accession For	
NSIS GRA&I	<input checked="" type="checkbox"/>
NSIS TAR	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

CONTENTS

	<u>Page</u>
INTRODUCTION	3
EXPERIMENTAL	5
Reaction Conditions and Work-Up Procedures	5
Analysis Procedures	6
Results and Discussion	7
CONCLUSIONS	21

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	HPLC TRACE OF COMPOUNDS ISOLATED FROM THE TNT-NaOCl REACTION	11

TABLES

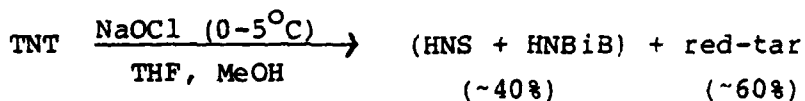
<u>Table</u>		<u>Page</u>
1	NMR DATA FOR COMPOUNDS ISOLATED FROM THE TNT-NaOCl REACTION	8
2	TLC DATA OF IDENTIFIED COMPOUNDS FROM THE HNS REACTION	9
3	HPLC DATA OF COMPOUNDS ISOLATED FROM THE TNT-NaOCl REACTION	10
4	COMPOUNDS IDENTIFIED FROM THE TNT-NaOCl REACTION ...	12
5	BY-PRODUCT REACTIONS WITH BASE IN SEVERAL SOLVENTS	17
6	TNT REACTIONS	19

INTRODUCTION

Since its discovery in the early 1960's by Kathryn G. Shipp, thermally stable 2,2',4,4',6,6'-hexanitrostilbene (HNS) has found numerous applications in military ordnance items¹ and throughout the aerospace industry^{2,3,4}.

HNS is currently prepared commercially⁵ by reacting 2,4,6-trinitrotoluene (TNT) with a 5% aqueous sodium hypochlorite solution (household bleach) in the presence of tetrahydrofuran (THF) and methanol (MeOH) as solvents (Shipp Process^{6,7}). It is assumed that, under the alkaline conditions of the reaction, TNT forms trinitrobenzyl anion, which is chlorinated to yield trinitrobenzyl chloride. Subsequent reaction of the chloride with alkali produces a mixture of HNS and HNBiB as crystalline products in a combined yield of less than 50% with the remainder of the material forming a red-tar fraction:

Shipp Process



¹Kilmer, E. E., "Hexanitrostilbene Recrystallized from Nitric Acid," NSWC/WOL TR 78-209, September 1979.

²Bement, L. J., "Application of Temperature Resistant Explosives to NASA Missions," presented at the Symposium on Thermally Stable Explosives at NSWC White Oak, Maryland, June 23-25, 1970.

³Rouch, L. L. and Maycock, J. N., NASA CR-2622, February 1976.

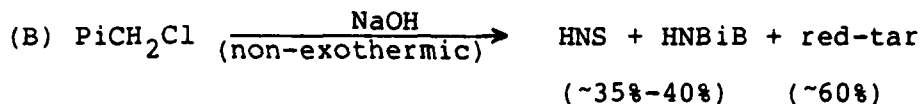
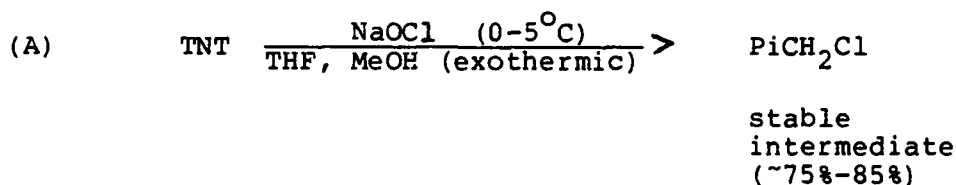
⁴Kilmer, E. E., J. Spacecraft, Vol. 1216, 1968, pp. 5, 10.

⁵Kilmer, E. E., "Overview of HNS. Production/Properties/Applications," NSWC TR 79-181, July 1979.

⁶Shipp, K. G. and Kaplan, L. A., J. Org. Chem., Vol. 31, 1966, p. 857.

⁷Shipp, K. G., J. Org. Chem., Vol. 29, 1964, p. 2620.

The purpose of this study is two-fold: (1) to determine what products, other than HNS and HNBiB, are produced by the TNT-NaOCl reaction, and (2) to search for a way to reduce or eliminate the concurrent side reactions which reduce the yield of HNS. An investigation of the composition of the red-tar fraction was necessary to determine the nature of the side reactions. Approximately 90% of the compounds contained in the red-tar fraction were isolated and characterized using thin layer chromatography (TLC) coupled with nuclear magnetic resonance spectroscopy (NMR), gas chromatography (GC), and/or high performance liquid chromatography (HPLC)^{8,9,10}. Final product identification was achieved by comparison with known compounds. To facilitate the second part of this study, the HNS reaction ($\text{TNT} \longrightarrow \text{HNS}$) was separated into two steps:



In Step A the stable intermediate, 2,4,6-trinitrobenzyl chloride (PiCH_2Cl), was obtained in a 75% - 85% yield by quenching the reaction mixture in dilute aqueous acid (HCl) approximately one minute after the NaOCl addition was complete. No evidence of appreciable amounts of by-products, other than unreacted TNT, was found by short stopping the reaction at this step. Since the red tar products are formed in Step B of the HNS reaction, this step was studied independently by investigating the PiCH_2Cl reaction with base in various solvents. In addition, several by-products of the Shipp reaction, 1,3,5-trinitrobenzene (TNB), 4,6-dinitro 2,1 benzisoxazole (Anil), 2,4,6-trinitrobenzyl alcohol (PiCH_2OH), 2,4,6-trinitrobenzaldehyde (PiCHO), and 2,4,6-trinitrobenzoic acid (PiCOOH), were also treated with base under different conditions to observe the products formed.

⁸ Kayser, E. G., "Analysis of 2,2',4,4',6,6'-Hexanitrostilbene (HNS) by High Performance Liquid Chromatography," NSWC/WOL TR 77-154, March 1975.

⁹ Stull, T. W., "Synthesis of High Purity Hexanitrostilbene," MHSMP-75-37, September 1975.

¹⁰ Schaffer, C. M., "HNS by Liquid Chromatography," MHSMP-77-51, 1977.

EXPERIMENTAL

Reaction Conditions and Work-Up Procedures

In order to determine the by-products which make up the red-tar fraction, a total of twenty TNT-NaOCl reactions were carried out under the conditions reported to give a maximum yield of HNS^{6,7}. The crystalline material (HNS-HNBiB) from each reaction was filtered from the reaction mixture, washed with methanol, dried and weighed. Further by-product reactions in the remaining filtrate were quenched by neutralization with aqueous HCl. After an initial extraction of the filtrate with benzene, both the extract and the remaining aqueous filtrate were evaporated to dryness and assayed by TLC and NMR for identifiable products. The organic components of the red-tar material contained in the benzene extract were separated using preparative TLC. After GC separation, the compounds were characterized by NMR, GC, and HPLC. Structural confirmation was achieved by comparison with authentic compounds.

Several of the TNT-NaOCl reactions were run in a closed system to retain any volatile compounds formed. Although several volatile materials were separated from both the benzene extract and the aqueous solution of the red-tar fraction, chloropicrin was the only volatile product that could be characterized and identified with GC and HPLC by comparison with the known compound.

A supplemental study of the reactions of TNT with several of the isolated by-products of the Shipp process (TNB, Anil, PiCH_2OH , PiCH_2Cl , PiCHO , and PiCOOH) was carried out at room temperature, with aqueous NaOH and NH_4OH , to observe the products formed. Reaction times were arbitrarily set at 30 and 90 minutes. A 1:1 mole ratio of reactant to base⁶ was used in each case, and MeOH, THF and dioxane were used as solvents. The work-up procedure for these reactions was identical to that used in the TNT-NaOCl reactions. The major reaction products were identified by NMR spectroscopy, and structural confirmation was achieved by comparison with authentic compounds.

^{6,7} See footnotes 6 and 7, page 3.

Analysis Procedures

Components of the organic red-tar material contained in the benzene extract were separated using preparative TLC. The plates (1/4" thickness) were prepared using Brinkman Silica gel HF 254 as the absorbent with a calcium sulfate binder. As purchased, this material contains a fluorescent indicator which allows location of the developed spots with a 254 nm light. The TLC developing solvents used were either benzene or a benzene:ether:ethanol mixture (50:30:20 by volume) depending on material polarity.

Estimated yields for HNS, HNBiB, unreacted TNT and nine by-products were obtained with a Varian HA-100 NMR spectrometer using 2,3-dimethyl-2,3-dinitrobutane as an internal standard. The chemical shift values (δ) for the TNT and by-product protons were determined relative to the reference compound, tetramethylsilane (TMS). The NMR solvent used was dimethyl sulfoxide- d_6 (min. isotopic purity 99.5 atom % D), since it was the best general solvent found for the TNT-NaOCl reaction products.

High performance liquid chromatography (HPLC) was also used to characterize the organic components from the benzene extract of the TNT-NaOCl reaction mixtures. A model ALC 202 liquid chromatograph equipped with a model 6000 solvent delivery system and a U6K high pressure loop injector (Waters Associates, Milford, Mass.) was used for the analyses and the eluent was continuously monitored with a 254nm UV detector. A Whatman HPLC guard column containing CO:PELL ODS pellicular material was used as a pre-column to the Whatman Partisil - 10 ODS-2 bonded octadecyl silane (C-18) reverse phase analytical column (25cm long, 4.6mm ID, 1/4" (6.350mm) OD). Typical efficiency of this analytical column, containing the (ODS) functionality, is 18,000 plates/meter. The UV absorption signals were recorded on an Omniscribe strip chart recorder set at 0.5cm/minute. The mobile phase consisted of MeOH (Baker - HPLC grade) and distilled water in a ratio of 2:3 by volume. Pressure at the column head was approximately 2000 psi with a flow rate of 2 ml/minute. The column temperature was approximately 25°C. All solvents and samples were filtered prior to use in the HPLC. Material concentration was determined by manually integrating the area of the chromatographic peak. Dimethylsulfoxide (DMSO, Fisher Scientific, A.C.S. grade) was used as the sample solvent. All the compounds, except PiCOOH at relatively low concentrations (<50 ppm), were found to be stable in the sample solvent (DMSO). In dilute solutions, PiCOOH reacts with DMSO to form TNB (peak retention time, 6.9 minutes). However, a peak retention time of approximately 1.0 minute was obtained with more concentrated PiCOOH-DMSO solutions. This value agrees with that obtained for PiCOOH in MeOH.

Results and Discussion

To date twelve compounds (HNS, HNBiB, Anil, PiOH, PiCH₂OH, PiCH₂Cl, chloropicrin, PiCOOH, PiCl, PiCHO, TNB, and TNT) extracted from the HNS synthesis reaction (Shipp Process) have been identified and characterized. Approximately 98% of the HNS is recovered in the crystalline form; however, several by-products and some unreacted TNT have been found trapped within the HNS crystal^{5,8,9,11}. In addition, all twelve compounds were found in the red-tar fraction. NMR and TLC data from all the compounds studied (with the exception of chloropicrin) are summarized in Tables 1 and 2. HPLC data are given in Table 3 and Figure 1.

Deuterium exchange experiments carried out earlier¹² indicated the formation of 2,4,6-trinitrobenzyl anion from 2,4,6-TNT in alkaline THF/MeOH solutions. The results of a recent photo-deuterium exchange study¹³ of aqueous 2,4,6-TNT solutions also indicate the initial formation of 2,4,6-trinitrobenzyl anion. Previous work at this laboratory by Burlinson, Kaplan, Adams and Sitzmann^{14,15} has shown that photolyzed aqueous solutions of TNT (using sunlight or a pyrex filtered HG-lamp) contain several of the compounds isolated from the TNT-NaOCl reaction (e.g., TNB, PiCHO, Anil, and PiCH₂OH).

Estimated weight percentages, based on NMR analysis, are reported for eleven of the organic components recovered from the red-tar fraction (Table 4). At least two other compounds formed in the reaction mixture but could not be identified due to their volatility at room temperature. The British (PERME Group at Waltham Abbey) have identified methyl nitrite as a volatile component of this reaction.

⁵See footnote 5, page 3.

^{8,9}See footnotes 8 and 9, page 4.

¹¹O'Keefe, D. M., "Digestion as a Process Aid for Hexanitrostilbene," SAND 76-0330, February 1977.

¹²Shipp, K. G., Kaplan, L. A., and Sitzmann, M. E., J. Org. Chem., Vol. 37, 1972, p. 1966.

¹³Burlinson, N. E., Sitzmann, M. E., Kaplan, L. A., and Kayser, E. G., J. Org. Chem., Vol. 44, 1979, pp. 21,3695.

¹⁴Burlinson, N. E., Kaplan, L. A., and Adams, C. E., "Photochemistry of TNT: Investigation of the 'Pink Water' Problem," NSWC/WOL TR 73-172, October 1973.

¹⁵Kaplan, L. A., Burlinson, N. E., and Sitzmann, M. E., "Photochemistry of TNT: Investigation of the 'Pink Water' Problem," NSWC/WOL TR 75-152, November 1975.

TABLE 1 NMR DATA FOR
COMPOUNDS ISOLATED FROM THE TNT- NaOCl REACTION

<u>Compound</u>	<u>NMR Spectrum</u> ^(a)
	δ
HNS	9.07 (s, 4 Ar-H) 7.11 (s, CH=CH)
HNBIB	9.05 (s, 4 Ar-H) 3.39 (s, $\text{CH}_2\text{-CH}_2$)
Pi CH_2Cl	9.05 (s, Ar-H) 4.98 (s, CH_2)
Pi CH_2OH	8.95 (s, 2 Ar-H) 4.82 (s, CH_2)
PiCHO	9.14 (s, 2 Ar-H) 10.51 (s, CH)
PiCOOH	9.11 (s, 2 Ar-H)
PiCl	9.20 (s, 2 Ar-H)
TNB	9.14 (s, 2 Ar-H)
PiOH	8.56 (s, 2 Ar-H)
TNT	8.98 (s, 2 Ar-H) 2.53 (s, CH_3)
Anil	10.56 (d, Ar-H) 9.31 (q, Ar-H) 8.62 (d, Ar-H)

(a) s=singlet, d=doublet, q=quartet, Ar=aromatic protons. Chemical shifts are in δ units downfield from internal TMS with line multiplicity and relative intensity in parentheses. Spectra were determined on a Varian HA-100 in DMSO-d_6 .

TABLE 2 TLC DATA^(a) OF
IDENTIFIED COMPOUNDS FROM THE HNS REACTION

<u>Compound</u>	<u>R_f (benzene)</u>
TNT	.86
PiCl	.89
PiOH	.17 ^(b)
PiCOOH	0.0 (origin)
PiCH ₂ Cl	.83
TNB	.74
PiCHO	.56
Anil	.64
PiCH ₂ OH	.20
HNS	.38
HNBiB	.58
Red-Tar (unidentified)	0.0 (origin)
<u>Compound</u>	<u>R_f (benzene:ether:ethanol) 50 : 30 : 20</u>
PiOH	.90
PiCOOH	.73
Red-Tar (unidentified)	0.0 - 0.05

(a) Thin layer plates prepared with Brinkman Silica gel - HF 254. Spot visualization by UV lamp. R_f taken from leading edge of spot.

(b) Streaking from .17 to origin.

TABLE 3 HPLC DATA OF
COMPOUNDS ISOLATED FROM THE TNT - NaOCl REACTION^(a)

<u>Compound</u>	<u>Peak Retention Time in Minutes</u>
PiCOOH	1.0
PiOH	1.1
DMSO ^(b)	1.7
PiCH ₂ OH	3.9
PiCHO	5.8
TNB	6.9
Anil	9.2
PiCl	12.0
TNT	12.8
Chloropicrin	18.5
PiCH ₂ Cl	19.8
HNS	38.5
HnBiB	58.6

(a) Column: Partisil-01-ODS-2 (reverse phase)
Mobile Phase: 40% MeOH/60% HOH by volume.
Flow Rate: 2 mls/minute.

(b) Sample Solvent: DMSO.

CONDITIONS
 COLUMN: PARTISIL-10-ODS-2
 (REVERSE PHASE)
 RATE: 2 ML/MINUTE
 MOBILE PHASE: 40% MeOH/60% HOH BY
 VOLUME
 SAMPLE SOLVENT: DMSO

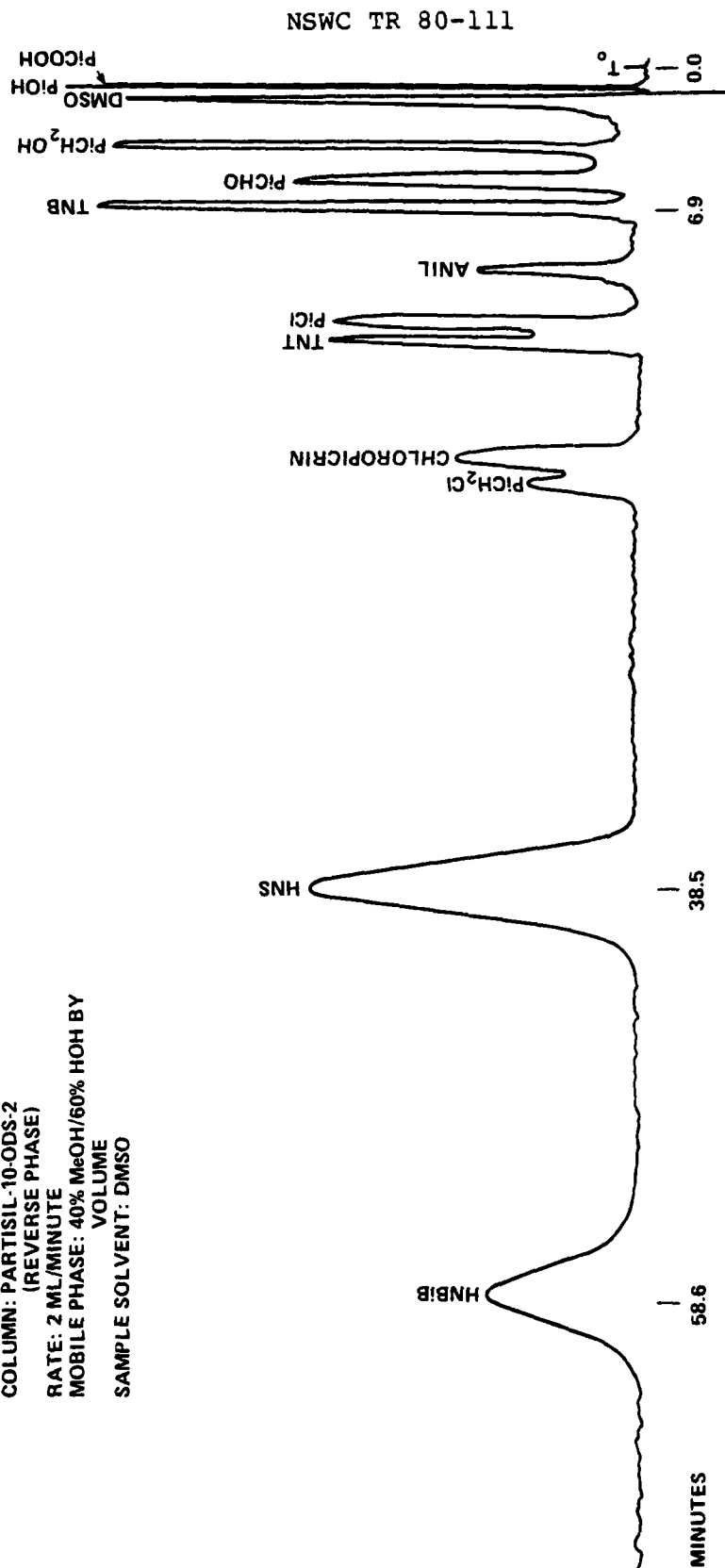


FIGURE 1 HPLC TRACE OF COMPOUNDS ISOLATED FROM THE TNT- NaOCl REACTION

TABLE 4 COMPOUNDS IDENTIFIED FROM THE TNT- NaOCl REACTION

<u>COMPOUND</u>	<u>% ESTIMATED YIELD</u>
	30-45
	5-10
	5-10

TABLE 4 COMPOUNDS IDENTIFIED FROM THE TNT- NaOCl REACTION (CONTINUED)

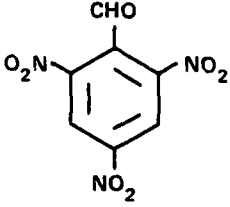
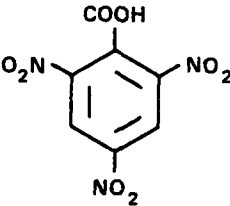
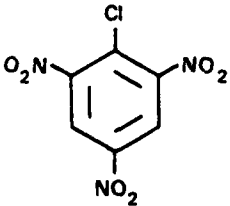
<u>COMPOUND</u>	<u>% ESTIMATED YIELD</u>
	
2, 4, 6 - TRINITROBENZALDEHYDE (PicHO)	~ 5-10
	
2, 4, 6 - TRINITROBENZOIC ACID (PicOOH)	0-8
	
PICRYL CHLORIDE (PicCl)	0-TRACE ^(a)

TABLE 4 COMPOUNDS IDENTIFIED FROM THE TNT- NaOCl REACTION (CONTINUED)

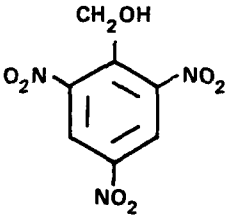
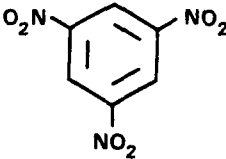
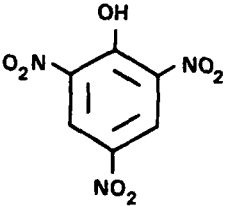
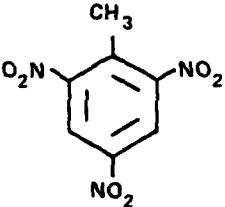
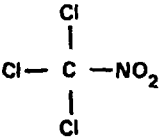
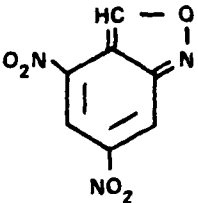
<u>COMPOUND</u>	<u>% ESTIMATED YIELD</u>
	
2, 4, 6 - TRINITROBENZYL ALCOHOL (PiCH_2OH)	5-10
	
1, 3, 5 - TRINITROBENZENE (TNB)	5-10
	
PICRIC ACID (PiOH)	0-TRACE ^(a)

TABLE 4 COMPOUNDS IDENTIFIED FROM THE TNT- NaOCl REACTION (CONTINUED)

<u>COMPOUND</u>	<u>% ESTIMATED YIELD</u>
	5-10
	>1-?
TRICHLORONITROMETHANE (CHLOROPICRIN) ^(b)	
	<1-5
4, 6 - DINITRO 2, 7 BENZISOXAZOLE 4, 6 - DINITROANTHRANIL (ANIL)	
RED-TAR ^(c)	5-10

Pi = 2, 4, 6 - TRINITROPHENYL

(a) TRACE = 1%

(b) MATERIAL NOT ACCURATELY DETERMINED DUE TO VOLATILITY AT ROOM TEMPERATURE

(c) UNIDENTIFIED MATERIAL - POSSIBLY HIGH MOLECULAR WEIGHT AND/OR POLAR MATERIAL

Approximately 5-10% of the red-tar fraction that remained in the aqueous filtrate after removal of the HNS/HNBiB crystals and extraction with benzene could not be identified. This material probably contains high molecular weight and/or polar compounds, since most of the unidentifiable segment (>50%) remained at the origin when chromatographed with the relatively polar solvent mixture, benzene:ether:ethanol (50:30:20 by volume).

Results of investigations of (a) the non-exothermic base reactions with aqueous sodium hydroxide (NaOH) and aqueous ammonium hydroxide (NH_4OH) in various solvents, and (b) the reactions of TNT with NaOCl in various solvents are summarized in Tables 5 and 6. In general, the base study indicated a greater degree of product reactivity in the aqueous NaOH system than in the aqueous NH_4OH system. As expected, the reactions of PiCH_2OH , PiCH_2Cl , and TNT with NaOH formed highly colored species and resulted in the greatest number of reaction products. However, most of the products resulting from the reaction of TNT with NaOH could not be separated or identified and remained at the origin when chromatographed with the relatively polar solvent mixture, benzene:ether:ethanol (50:30:20 by volume). Approximately 5-15% HNBiB was isolated from the TNT-NaOH reaction mix. Both TNB and anil proved to be stable end products under these reaction conditions. Trinitrobenzoic acid (PiCOOH) decarboxylates to TNB in the presence of base. This reaction also occurs quite rapidly in DMSO (without added base) at PiCOOH concentrations of less than 50 ppm.

TNB is also the final product from trinitrobenzylaldehyde (PiCHO). This reaction^{16,17} proved to be quantitative in several of the solvents investigated. As expected, the reaction of trinitrobenzyl chloride (PiCH_2Cl) with NaOH produced the highest yield of HNS (35-45%) in the THF-MeOH (2:1) and the THF solvent systems (Table 5). This is also true of the TNT-NaOCl reactions (Table 6). None of the other solvents examined exhibited the apparent specificity of THF for this reaction.

¹⁶Secareanu, S., Ber. Dtsch. Chem. Ges., Vol. 64, 1931, p. 837.

¹⁷Secareanu, S., Bull. Soc. Chim., Vol. 51, 1931, p. 591.

TABLE 5 BY-PRODUCT REACTIONS WITH BASE IN SEVERAL SOLVENTS

BY PRODUCT REACTANT	BASE	SOLVENT SYSTEM	REACTION TIME (IN MINUTES)	TEMPERATURE °C	% REACTION PRODUCTS									
					PiCH ₂ OH	PiCHO	ANIL	TNB	POH	TNT	PiCOOH	PiCH ₂ Cl	HNS	HNBIB
PiCH ₂ OH	NaOH	THF/MeOH (2:1)	30	22.5°-25°	28	12	19	17	2					
PiCH ₂ OH	NaOH	THF/MeOH (2:1)	90	22.5°-25°	17	21	16	12	2					
PiCH ₂ OH	NaOH	MeOH	90	22.5°-25°	15	2	14	30						
PiCH ₂ OH	NaOH	DIOXANE	90	22.5°-25°	19	5	5	3	26					
PiCH ₂ OH	NaOH	DIOXANE	90	22.5°-25°	19	2	2	5	28					
PiCH ₂ OH	NaOH	DIOXANE (DISTILLED)	90	22.5°-25°	22	10	6	20						
PiCH ₂ OH	NaOH	THF	90	22.5°-25°	19	25	10	9						
PiCH ₂ OH	NH ₄ OH	THF/MeOH (2:1)	90	22.5°-25°	71									
PiCH ₂ OH	NH ₄ OH	DIOXANE	90	22.5°-25°	45									
PiCH ₂ OH	NH ₄ OH	MeOH	90	22.5°-25°	73									
PiCH ₂ Cl	NaOH	THF/MeOH (2:1)	30	22.5°-25°	5	9	~1	2	~1			28	36	~10
PiCH ₂ Cl	NaOH	THF/MeOH (2:1)	90	22.5°-25°	5	6	~1	2	~1			17	46	~3
PiCH ₂ Cl	NaOH	MeOH	90	22.5°-25°	5			11				24	10	
PiCH ₂ Cl	NaOH	DIOXANE	90	22.5°-25°	2	5		<1	15			26	17	~1
PiCH ₂ Cl	NaOH	DIOXANE (DISTILLED)	90	22.5°-25°	6	7	2	4				15	15	
PiCH ₂ Cl	NaOH	THF	90	22.5°-25°	4	7	~4	~4	~1			15	40	~5
PiCH ₂ Cl	NH ₄ OH	THF/MeOH (2:1)	90	22.5°-25°	3	5		2				51	16	5
PiCH ₂ Cl	NH ₄ OH	DIOXANE	90	22.5°-25°	2							52		
PiCH ₂ Cl	NH ₄ OH	MeOH	90	22.5°-25°	5	3		5				47	~1	
PiCHO	NaOH	THF/MeOH (2:1)	30	22.5°-25°		40		18						
PiCHO	NaOH	THF/MeOH (2:1)	90	22.5°-25°		22		68						
PiCHO	NaOH	MeOH	90	22.5°-25°		<5		85						
PiCHO	NaOH	MeOH	90	22.5°-25°		~2		95						
PiCHO	NaOH	DIOXANE	90	22.5°-25°		45		31						
PiCHO	NaOH	THF	90	22.5°-25°		55		40						
PiCHO	NH ₄ OH	THF/MeOH (2:1)	90	22.5°-25°		60		20						
PiCHO	NH ₄ OH	DIOXANE	90	22.5°-25°		88								
PiCHO	NH ₄ OH	MeOH	90	22.5°-25°				98						

TABLE 5 (CONTINUED) BY-PRODUCT REACTIONS WITH BASE IN SEVERAL SOLVENTS

BY-PRODUCT REACTANT	BASE	SOLVENT SYSTEM	REACTION TIME (IN MINUTES)	TEMPERATURE °C	% REACTION PRODUCTS										
					PiCH ₂ OH	PiCHO	ANIL	TNB	PiOH	TNT	PiCOOH	PiCH ₂ Cl	HNS	HNBIB	
PiCOOH	NaOH	THF/MeOH (2:1)	30	22.5°-25°				15				59			
PiCOOH	NaOH	THF/MeOH (2:1)	90	22.5°-25°				15				53			
PiCOOH	NaOH	MeOH	90	22.5°-25°				6				80			
PiCOOH	NaOH	DIOXANE	90	22.5°-25°				19				41			
PiCOOH	NaOH	THF	90	22.5°-25°				8				47			
PiCOOH	NH ₄ OH	THF/MeOH (2:1)	90	22.5°-25°				40				48			
PiCOOH	NH ₄ OH	DIOXANE	90	22.5°-25°				11				61			
PiCOOH	NH ₄ OH	MeOH	90	22.5°-25°				~1				90			
TNB	NaOH	THF/MeOH (2:1)	90	22.5°-25°				90							
TNB	NaOH	MeOH	90	22.5°-25°				95							
TNB	NaOH	THF	90	22.5°-25°				89							
TNB	NH ₄ OH	THF/MeOH (2:1)	90	22.5°-25°				85							
TNB	NH ₄ OH	THF	90	22.5°-25°				90							
TNB	NH ₄ OH	MeOH	90	22.5°-25°				96							
ANIL	NaOH	THF/MeOH (2:1)	90	22.5°-25°					75						
ANIL	NaOH	MeOH	90	22.5°-25°					80						
ANIL	NaOH	DIOXANE	90	22.5°-25°					15						
ANIL	NaOH	THF	90	22.5°-25°					68						

BY-PRODUCT/BASE REACTION MIXTURES:
TO A SOLUTION OF 0.0042 MOLES OF REACTANT IN 16.92 ML THF AND 8.46 ML MeOH (AT AMBIENT TEMPERATURE) IS ADDED 16.92 ML
OF WATER CONTAINING 0.0042 MOLES OF EITHER NaOH OR NH₄OH.

REACTION TIME: 30 AND/OR 90 MINUTES

MAJOR IDENTIFIABLE REACTION PRODUCTS: DETERMINED BY NMR SPECTROSCOPY

NMR SAMPLE SOLVENT: DMSO

TABLE 6 TNT REACTIONS

REACTANT	NaOCI	BASE	SOLVENT SYSTEM	REACTION TIME IN MINUTES	TEMPERATURE °C	% REACTION PRODUCTS			
						TNT	TNB	HNS	HNBiB
TNT		NaOH	THF/MeOH (2:1)	30	22.5°-25°	53	<1	TRACE	6
TNT		NaOH	MeOH	90	22.5°-25°	37			6
TNT		NaOH	DIOXANE	90	22.5°-25°	16			16
TNT		NaOH	THF	90	22.5°-25°	29			18
TNT		NH ₄ OH	THF/MeOH (2:1)	90	22.5°-25°	74			
TNT		NH ₄ OH	DIOXANE	90	22.5°-25°	39			
TNT		NH ₄ OH	MeOH	90	22.5°-25°	65			
TNT	NaOCI		THF/MeOH (2:1)	2-3 20	<15° 22.5°-25°			43	8
TNT	NaOCI		THF/MeOH (2:1)	5 30	<15° 22.5°-25°			38	10
TNT	NaOCI		THF/MeOH (2:1)	2-3 20	<15° 22.5°-25°			35	7
TNT	NaOCI		THF	2-3 20	<15° 22.5°-25°			41	6
TNT	NaOCI		DIOXANE	2-3 20	<15° 22.5°-25°			~12	<5
TNT	NaOCI		MeOH	2-3 20	<15° 22.5°-25°			~2	
TNT	NaOCI		ACETONE	2-3 20	<15° 22.5°-25°			<2	~2
TNT	NaOCI		ACETONITRILE	2-3 20	<15° 22.5°-25°			1-2	

TNT/BASE REACTION MIXTURES:

TO A SOLUTION OF 0.0042 MOLES OF TNT IN 16.92 ML THF AND 8.46 ML MeOH (AT AMBIENT TEMPERATURE) IS ADDED 16.92 ML OF WATER CONTAINING 0.0042 MOLES OF EITHER NaOH OR NH₄OH.
REACTION TIME: 30 AND/OR 90MINUTES

TNT/NaOCI REACTION MIXTURES:

1.0 GM (0.0044 MOLES) OF TNT IN (10 ML THF AND 5 ML MeOH) IS CHILLED TO ABOUT 0°C THEN ADDED QUICKLY, WITH THOROUGH MIXING, TO 10 ML OF "CHLOROX" (COMMERCIAL BLEACH - 5.25%) WHICH IS ALSO CHILLED TO 0°C. DURING THE INITIAL REACTION PERIOD OF ABOUT 2-3 MINUTES, THE TEMPERATURE OF THE MIXTURE IS HELD BELOW 15° C BY CHILLING IN AN ICE-SALT BATH. THE MIXTURE IS THEN ALLOWED TO STAND AT AMBIENT TEMPERATURE UNTIL PRECIPITATION OF THE HNS PRODUCT IS COMPLETE (APPROXIMATELY 20-30 MINUTES).

MAJOR IDENTIFIABLE REACTION PRODUCTS: DETERMINED BY NMR SPECTROSCOPY
NMR SAMPLE SOLVENT: DMSO

CONCLUSIONS

The by-products isolated from the Shipp Hexanitrostilbene (HNS) Process are: hexanitrobibenzyl (HNBiB), trinitrobenzene (TNB), trinitrobenzoic acid (PiCOOH), 4,6-dinitro 2,1 benzisoxazole (Anil), trinitrobenzaldehyde (PiCHO), trinitrobenzyl chloride (PiCH₂Cl), picryl chloride (PiCl), picric acid (PiOH), trinitrobenzyl alcohol (PiCH₂OH), and trichloronitromethane (chloropicrin). Some unreacted TNT (5-10%) was also isolated from the red-tar fraction of the reaction. The investigation of the reactions of all of the above polynitroaromatic compounds with base furnished some additional information, but no method was found to either reduce the side reactions or increase the yield of HNS. None of the solvents investigated displayed the pronounced specificity of tetrahydrofuran (THF) for this reaction.

REFERENCES

1. Kilmer, E. E., "Hexanitrostilbene Recrystallized from Nitric Acid," NSWC/WOL TR 78-209, September 1979.
2. Bement, L. J., "Application of Temperature Resistant Explosives to NASA Missions," presented at the Symposium on Thermally Stable Explosives at NSWC White Oak, Maryland, June 23-25, 1970.
3. Rouch, L. L. and Maycock, J. N., NASA CR-2622, February 1976.
4. Kilmer, E. E., J. Spacecraft, Vol. 1216, 1968, pp. 5, 10.
5. Kilmer, E. E., "Overviews of HNS. Production/Properties/Applications," NSWC TR 79-181, July 1979.
6. Shipp, K. G. and Kaplan, L. A., J. Org. Chem., Vol. 31, 1966, p. 857.
7. Shipp, K. G., J. Org. Chem., Vol. 29, 1964, p. 2620.
8. Kayser, E. G., "Analysis of 2,2',4,4',6,6'-Hexanitrostilbene (HNS) by High Performance Liquid Chromatography," NSWC TR 77-154, March 1975.
9. Stull, T. W., "Synthesis of High Purity Hexanitrostilbene," MHSMP-75-37, September 1975.
10. Schaffer, C. M., "HNS by Liquid Chromatography," MHSMP-77-51, 1977.
11. O'Keefe, D. M., "Digestion as a Process Aid for Hexanitrostilbene," SAND 76-0330, February 1977.
12. Shipp, K. G., Kaplan, L. A., and Sitzmann, M. E., J. Org. Chem., Vol. 37, 1972, p. 1966.
13. Burlinson, N. E., Sitzmann, M. E., Kaplan, L. A., and Kayser, E. G., J. Org. Chem., Vol. 44, 1979, pp. 21, 2695.
14. Burlinson, N. E., Kaplan, L. A., and Adams, C. E., "Photochemistry of TNT: Investigation of the 'Pink Water' Problem," NOLTR 73-172, October 1973.

REFERENCES (continued)

15. Kaplan, L. A., Burlinson, N. E., and Sitzmann, M. E., "Photochemistry of TNT: Investigation of the 'Pink Water' Problem," NSWC/WOL TR 75-152, November 1975.
16. Secareanu, S., Ber. Dtsch. Chem. Ges., Vol. 64, 1931, p. 837.
17. Secareanu, S., Bull. Soc. Chim., Vol. 51, 1932, p. 591.

DISTRIBUTION

	<u>Copies</u>
Commander Naval Sea Systems Command Attn: SEA-62R32 SEA-62R SEA-09G32 (Technical Library) Department of the Navy Washington, D. C. 20362	2
Office of Naval Research Attn: ONR-175 (Technical Library) ONR-473 (R. Miller) 801 N. Quincy Street Arlington, VA 22217	2
Chief of Naval Operations Washington, D. C. 20350	
Commander Naval Weapons Center Attn: Technical Library China Lake, CA 93555	
Commanding Officer Naval Ordnance Station Attn: W. Carr Indian Head, MD 20640	
Commanding Officer Naval Academy Attn: Hd. Weps Dept Annapolis, MD 21402	
Superintendent Naval Postgraduate School Monterey, CA 93940	
Commanding Officer Naval Weapons Station Attn: Technical Library W. McBride Yorktown, VA 23491	

NSWC TR 80-111

DISTRIBUTION (Cont.)

Copies

Commanding Officer
Naval Weapons Support Center
Crane, IN 47522

Director
Strategic Systems Projects Office
Attn: SSPO-2731 (M. Baron)
Department of the Navy
Washington, D. C. 20376

Commander
Naval Air Systems Command
Attn: AIR-1116
Washington, D. C. 20361

Commanding Officer
Ballistics Research Laboratory
Attn: Technical Library
Aberdeen Proving Ground
Aberdeen, MD 21005

Commanding General
Army Materiel Command
Department of the Army
Washington, D. C. 20316

Commander
Army Rocket and Missile Agency
Redstone Arsenal
Huntsville, AL 35809

Director
Defense Technical Information Center
Attn: TIPCR
Cameron Station
Alexandria, VA 22314

12

Commander
Systems Engineering Group
Attn: RTD
Wright-Patterson Air Force Base, OH 45433

Chief of Staff
U. S. Air Force
Attn: AFORD-AR
Washington, D. C. 20350

NSWC TR 80-111

DISTRIBUTION (Cont.)

Copies

Lyndon B. Johnson Space Center
National Aeronautics & Space Administration
Attn: Technical Library
T. Graves/EP4
2101 Webster-Seabrook Road
Houston, TX 77058

George C. Marshall Space Flight Center
National Aeronautics & Space Administration
Attn: Technical Library
Robert White/EP-14
Huntsville, AL 35812

University of California
Lawrence Livermore National Laboratory
Attn: Milton Finger
Walter Selig
P.O. Box 808
Livermore, CA 94550

Chemtronics
Attn: Technical Library
Heather Hudson
Old Bee Tree Road
Swannanoa, NC 28778

Ensign Bickford Company
Attn: B. Boggs
660 Hopmeadow Street
Simsbury, CT 06070

Explosive Technology
Attn: F. Burkdoll
P.O. Box KY
Fairfield, CA 94533

General Dynamics
Attn: W. Early (MZ2843)
K. Monroe
P.O. Box 748
Fort Worth, TX 76101

Grumman Aerospace Corporation
Attn: J. Hopkins
South Oyster Bay Road
Bethpage, NY 11714

NSWC TR 80-111

DISTRIBUTION (Cont.)

Copies

Teledyne McCormick Selph
Attn: R. Richards
P.O. Box 6
Hollister, CA 95023

Lockheed Missiles & Space Co. , Inc.
Attn: F. Chapman
P.O. Box 504
Sunnyvale, CA 94086

Los Alamos Scientific Laboratory
Attn: Dr. L. Smith
P.O. Box 1663
Los Alamos, NM 87544

McDonnell Douglas Corporation
Attn: M. Schimmel
P.O. Box 516
St. Louis, MO 62166

Ordnance Engineering Associates
Attn: Ahmed Kafadar
1030 East North Avenue
Des Plains, IL 60016

Sandia Corporation
Attn: Dr. N. Brown
P.O. Box 5400
Albuquerque, NM 87115

Space Ordnance Systems, Inc.
Attn: Dr. N. Zable
375 Santa Trinita
Sunnyvale, CA 94006

Langley Research Center
National Aeronautics & Space Administration
Attn: L. Bement
W. Kellier
R. Brooks
Hampton, VA 23665

Mason & Hanger-Silas Mason Company, Inc.
Pantex Plant
Attn: Dr. Clyde Alley
Ted Stull
P.O. Box 30020
Amarillo, TX 79177

NSWC TR 80-111

DISTRIBUTION (Cont.)

Library of Congress
Washington, DC 20540
Attn: Gift and Exchange Division

Copies

4

TO AID IN UPDATING THE DISTRIBUTION LIST
FOR NAVAL SURFACE WEAPONS CENTER, WHITE
OAK TECHNICAL REPORTS PLEASE COMPLETE THE
FORM BELOW:

TO ALL HOLDERS OF NSWC/TR 80-111
by Eleanore G. Kayser, Code R11

DO NOT RETURN THIS FORM IF ALL INFORMATION IS CURRENT

A. FACILITY NAME AND ADDRESS (OLD) (Show Zip Code)

NEW ADDRESS (Show Zip Code)

B. ATTENTION LINE ADDRESSES:

C.

☐ REMOVE THIS FACILITY FROM THE DISTRIBUTION LIST FOR TECHNICAL REPORTS ON THIS SUBJECT.

D.

NUMBER OF COPIES DESIRED